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Impact of Coal and Oil Shale Products on Gasoline Composition 1976-2000 Task One

Southwest Research Inst, San Antonio, Tex Mobile Energy Div

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IMPACT OF COAL AND OIL SHALE PRODUCTS ON GASOLINE COMPOSITION 1976-2000 TASK ONE FINAL REPORT

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Mobile Source Air Pollution Control
Emission Control Technology Division
Ann Arbor, Michigan 48105

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A consensus assessment is made of the impact of coal- and oil shale-derived crudes upon the composition of gasoline. It is concluded that this impact will be negligible, since the most promising area for utilization of such crudes will be as burner fuels and middle distillates. Such utilization of coal and oil shale resources will in turn reduce the demand on petroleum resources which will continue to be the principal source of gasoline for the remainder of the 20th century.

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SUMMARY

This report covers Task 1 of a 5-task study intended to identify emissions from coal- and oil shale-derived gasolines. The fundamental goal of Task 1 has been to define "best estimates" for composition and properties of such gasolines for the time frame 1976-2000. The principal source of relevant information for this projection was a comprehensive series of personal interviews with industrial and governmental personnel directly involved in resource, process and automotive developmental efforts. This report is intended as a consensus resulting from these interviews.

It should be pointed out that the opinions summarized herein were neither (a) unanimous nor (b) ill-considered. The individuals contacted were specifically chosen for their experience and current involvement in marketing and/or technology forecasting for fuels and powerplants development. An effort was made to cover the entire spectrum of each concerned industry. Consequently, for virtually every statement or opinion reflected herein there is, somewhere, an opposing view albeit a minority one.

The most significant generalization resulting from this study is that *the impact of coal and oil shale products on gasoline composition and properties during 1976-2000 will be negligible.* There are three principal reasons for this conclusion:

(1) The projected total quantity of crude production resulting from coal or oil shale processes in 1976-2000 will be only a small fraction of conventional petroleum crude production (see Figure 1)*.

(2) Anticipated use of coal and oil shale crudes is for burner fuels, middle distillates, etc., which will reduce the demand on petroleum resources, thus freeing more petroleum crude for refining into automotive gasoline. Whereas gasoline may have some constituents theoretically traceable to coal or oil shale crude as a result of refinery blend-off, these materials are not expected to constitute more than 3 to 4 percent of total production by 2000 AD (see Figure 2)* and will be indistinguishable from similar petroleum-derived constituents.

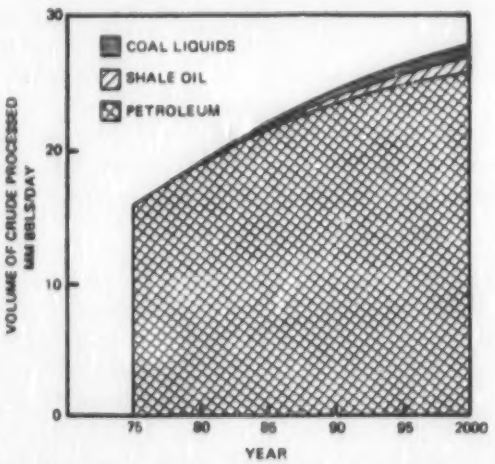

FIGURE 1. PROJECTED VOLUMES OF PROCESSED CRUDE FROM VARIOUS SOURCES

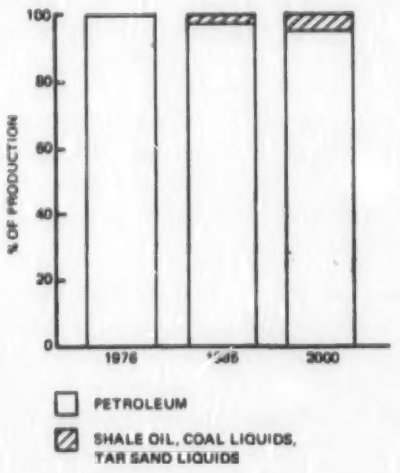

FIGURE 2. PROJECTED CRUDE SOURCES FOR GASOLINE PRODUCTION

*Figures 1 and 2 are intended as consensus portrayals of crudes production, and, as such, cannot be referenced to a single source.

(3) Automotive engine technology development, more so than an emerging synfuels industry, will be the overriding factor in tailoring gasoline composition/performance. The conventional spark-ignition engine is expected to continue to dominate the private automobile market for the balance of this century. Technological improvements in fuel economy and emissions control may require changes to existing fuel specifications which can probably be accommodated by the refinery industry.

Assuming that crudes derived from coal and oil shale will have no significant impact on gasoline composition, the next logical question is: *what will gasoline composition be*? Table 1 presents principal properties and compositional ranges which exist today and those projected for 1985 and 2000. The summer/winter distillation and vapor pressure values shown for present gasolines are the limits for fuels to be used in extremely hot or extremely cold environments, the average summer fuels being somewhat more volatile (10 to 11.5 lb), and the average winter fuels less volatile (11.5 to 13 lb). These limits have been established by the American Society for Testing and Materials and by Federal specifications. The compositional analysis data represents a range of values obtained from samplings of several nationwide gasoline surveys (refinery and service station samples) reported from 1969 to 1976. Based on regulations promulgated by EPA in the *Federal Register*, Vol. 41, No. 164, Monday, August 23, 1976, and on activities of the State of California Air Resources Board as reported on December 9, 1975 in the report entitled, "The Feasibility and Impact of Reducing Emissions by Reducing Gasoline Volatility," it is logical to expect that volatility of gasolines will be reduced in order to meet evaporative emission requirements for vehicles and service stations. This will be accomplished by the reduction in concentration of the lighter hydrocarbons, butanes, and pentanes. These hydrocarbons serve a far more valuable purpose as constituents in other petrochemical processes. Benzene, toluene, and xylenes serve to increase octane number and either occur naturally as a result of specific gasoline-producing processes or are added to the blend. Concentration of benzene and toluene will intentionally be reduced in this time frame since they, too, can be put to better use in the petrochemical industry. Octane levels will likely be maintained by increasing the concentration of isometric C_6–C_7 hydrocarbons. The heavier C_9+ aromatic compounds, which also serve to increase octane number, will remain relatively constant.

TABLE 1. PROJECTED GASOLINE COMPOSITION AND PROPERTIES

Distillation, °F	Present		1985	2000
	Summer	Winter		
10% evap	158 max	122 max	140-165	140-165
50% evap	170-250	170-230	180-250	180-250
90% evap	374 max	365 max	374 max	374 max
End point	437 max	437 max	450 max	450 max
Reid Vapor Pressure, max, lb	9	15	6	6
C_4-C_5, vol %	12-20		5-8	5-8
C_6-C_7, vol %	17-36		20-40	20-40
Benzene, vol %	0.5-2.1		<0.5	---
Toluene, vol %	0.6-14.1		<10	<10
Xylenes, vol %	1.0-13.6		10-20	15-20
C_9+ aromatics, vol%	1.1-20.1		10-20	13-18

Lower volatility will cause harder starts and longer warmup in present day engines, although vapor lock and hot start problems due to high volatility fuel will be virtually eliminated. It is anticipated, however, that engine manufacturers will modify carburetion or adopt fuel injection more extensively so that performance problems associated with fuel volatility will be minimized. The traditional mechanism of refining industry response to automotive industry specification is expected to continue.

The essential theme of this report is that gasoline will remain primarily a petroleum-derived product through 2000 A.D. The material in the main body of the report is intended to provide details of coal and oil shale crude composition, candidate conversion processes, and to discuss those technological factors which will influence development of these energy resources.

I. INTRODUCTION

Domestic production of petroleum oil and gas continues to decline while demand increases. The lack of economic incentives inhibits exploration and recovery of more reserves. In this event, the only alternative is the development of other types of energy sources. Most obviously there is coal, a tremendously abundant hydrocarbon source material underlying vast areas of the nation. Next there is oil shale, a rock containing a hydrocarbon material which can be thermally treated to produce an oil very similar to conventional petroleum. On a far smaller scale there exists the possibility of using oil extracted from tar sands.

While many improvements have yet to be made in efficiency, existing technology is capable of converting all of these resources into liquid forms of energy. The reason this conversion is not presently being done is that it is more difficult, and therefore more expensive, to make liquid fuel from coal, oil shale, and the other resources than from petroleum crude oil which is available by conventional drilling.

The factors which cause synthetic fuels from coal, oil shale, and tar sands to be more expensive consist of more than just the degree of processing required. In particular, they relate to government policies and incentives. From a purely technical point of view, dollar-for-dollar, liquid fuels could probably be produced from coal and oil shale at about the same cost as the price we are now paying for foreign crude. Because of the risks involved in building plants for this purpose, however, investors are not willing to provide the necessary capital. The risk of plant failure is small; but there is a remote possibility foreign prices could drop, thus making the synthetic fuels plant a white elephant. The absence of government guarantees makes it likely that investment capital will not be available for synthetic fuel plants in the near future.

In the event that a financial subsidy is provided at some future date for the manufacture of gasoline exclusively from coal or oil shale resources, the cost of an initial batch of such synfuel would be too high for public consumption. The obvious candidate for field evaluation of this new fuel would be a government fleet—likely the military or a civilian federal fleet. A natural and mandatory part of this fleet test evaluation would be measurement of exhaust emissions which, in a well-designed experimental program, would result in direct comparison with control vehicles operated on petroleum-derived gasoline. It is possible, therefore, that some fuel-emissions relationships would be defined in advance of general adoption of synfuel-based technology. Identification of trace contaminants would likely not be a part of such an advance fleet test.

Technology is currently available to convert coal, oil shale and tar sands into synthetic crudes which, in turn, can be refined into clean liquid fuels. Each of these sources of hydrocarbons must be treated differently to produce useful products and should be discussed separately. The retorting of oil shale results in a viscous, high molecular weight syncrude which could be refined into gasoline and diesel and jet fuels similar in composition to products derived from petroleum crudes. Conversion of coal to liquid fuels can be accomplished by many specific processes, which can be categorized into four general types. Three of these process types yield viscous, high molecular weight syncrudes, generally high in aromatics and sulfur content, which require considerable refining to yield clean liquid fuels. The fourth type is an indirect liquefaction process whereby hydrocarbon gases derived from coal are polymerized into liquid fuels. Other fuels that can be economically derived from coal are methane and methanol; however, a discussion of these products is beyond the scope of this work. Syncrudes extracted from tar sands are also viscous and high in sulfur, although in

Canada the Athabasca tar sands syncrude is blended with petroleum crude for nearby refinery feed stocks. Thus, most of the syncrudes derived from oil shale, coal and tar sands will be viscous, high molecular weight materials containing sulfur, nitrogen and other nonhydrocarbon impurities, and will require severe refinery processing to yield clean liquid fuels such as gasoline, kerosene and diesel fuels. Economic considerations may dictate their use as boiler fuels, heating oils or petrochemical feedstocks where less refining is required. By using them for this purpose, large quantities of petroleum crude oil now being used in these applications could be refined into gasoline, kerosene and diesel fuels. *If cost is not a constraint to convert these syncrudes into gasoline, the physical and chemical properties of the product could be made virtually identical to those of gasoline produced from conventional petroleum crude.*

Since this report deals specifically with the potential production of gasoline derived from coal and oil shale, it should be noted that:

- Syncrude from shale will probably be used for manufacturing boiler fuels, as petrochemical feedstocks, or, at most, blending with conventional petroleum crude for refining into gasoline and other fuels.

- Syncrude from certain coal conversion processes will be utilized much the same as shale oil syncrude.

- Indirect liquefaction utilizing the Fischer-Tropsch process produces low molecular weight hydrocarbons identical to those occurring in petroleum derived gasoline. This process is in commercial operation in South Africa.

- Syncrude production from tar sands will be minimal in this country; however, any production will probably be blended with conventional crude for refining into fuels.

The above observations indicate that the production of gasoline in the U.S. from oil shale syncrude is a remote possibility, while gasoline from coal is more probable. In any event, a knowledge of any adverse environmental effects from burning such fuels is important. The first step in evaluation of emission compositions would be estimations of the compositional ranges of fuels produced from specific source materials and processes felt to be representative of syncrude technology.

II. RESOURCES

The following is a brief discussion on each of the principal sources for raw materials from which gasoline could be synthesized.

A. Oil Shale

Oil shale is a fine-grain sedimentary rock containing a solid organic material called kerogen, which is released from shale when the rock is heated. Gaseous fractions as well as a heavy liquid can be recovered, and the liquid can be upgraded to a syncrude, equivalent to a high-grade crude oil. Deposits of oil shale are found in layers called zones, sandwiched between other layers of sedimentary rock.

Oil shale is found over a wide area of the U.S., but the richest deposits, which are at least 10-ft thick and yield on the average 25 gallons or more of oil per ton of oil shale, are located in the Green River Formation spanning Colorado, Utah, and Wyoming. In fact, 90 percent of the identified oil shale resources of the U.S. are located in the Green River Formation (Figure 3). The rich deposits in this formation (Table 2) cover roughly 17,000 square miles and contain an estimated 4 trillion

TABLE 2. OIL RESERVES IN KNOWN DEPOSITS IN THE GREEN RIVER FORMATION BILLION BARRELS OF OIL EQUIVALENT

Shale Grade, gal. oil/ton	Piceance Creek Basin, Colorado	Uinta Basin Utah	Green River Basin, Wyoming
25-65	450-500	90	30
10-25	800	230	400
5-10	200	1,500	300
Area totals	1,500	1,820	730
(Formation total = 4,050)			

FIGURE 3. DISTRIBUTION OF U.S. OIL SHALE RESOURCES

barrels of oil equivalent. Distribution of reserves among the three basins which comprise the Green River Formation is shown in Table 2.

B. Coal

The total remaining reserve of coal in the U.S. is estimated at 3.2×10^{12} tons, of which about 50 percent has not actually been identified but is surmised to exist on the basis of broad geological knowledge and theory. Roughly 360×10^9 tons of known reserves are surface mineable and 553×10^9 tons are recoverable by current technology. The surface mineable characteristics of known western subbituminous and lignite coal reserves make them attractive for future liquefaction operations. Thus about 687×10^9 tons of known coal resources await both technological advances in recovery techniques and a receptive market.

TABLE 3. RANK OF IDENTIFIED U.S. COAL RESOURCES

Rank	Identified Resources (billions of tons)*
Anthracite	21
Bituminous	686
Subbituminous	424
Lignite	449
Total	1580

Source: Averitt, 1973:137.

*In short tons (2000 lb).

The classification of coals is based on compositional characteristics such as fixed carbon content, heating value, and impurities. Anthracite and bituminous coals contain more carbon than other types and are ranked on this basis (Figure 4). Subbituminous and lignite or brown coal are ranked on the basis of heating value as shown in Figure 5. Anthracite and bituminous coals make up about 45 percent of the identified U.S. resources while subbituminous and lignite make up the balance of 55 percent (Table 3).

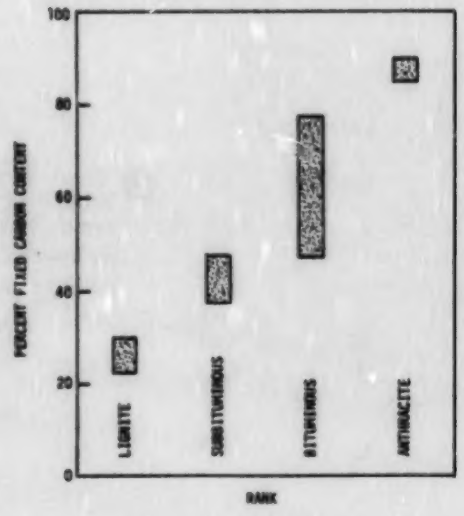

FIGURE 4. FIXED CARBON CONTENT OF MAJOR COAL RANKS

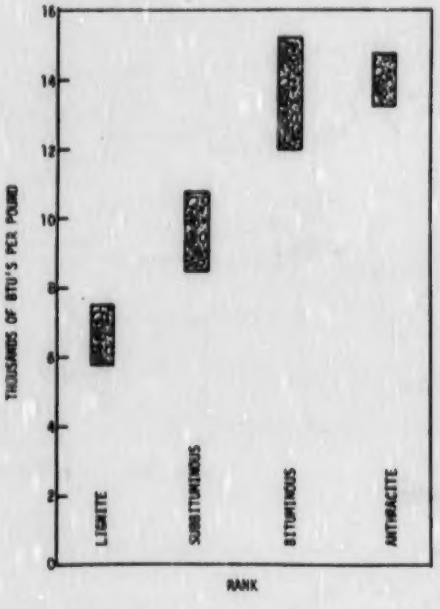

FIGURE 5. HEAT CONTENT OF MAJOR COAL RANKS

Coals are also graded on the basis of moisture and other impurities such as ash and sulfur. Moisture content is related to rank inasmuch as the higher the rank, the lower the moisture content. Some anthracites contain 1 percent moisture while some lignites have as much as 40 percent moisture. Ash content can vary in samples from the same seam, and investigators have found that, throughout the U.S., ash content ranges from 2.3 to 33 percent. Sulfur compounds are present in coal, and range in concentration from 0.2 to 7.0 percent sulfur. The presence of sulfur compounds in the coal resource is important from several aspects, not the least of which are environmental considerations in the conversion process and in the combustion of the finished fuel. The low-sulfur coal (1 percent or less) is predominantly found in the western area of the country, while the high-sulfur coals are more common in the eastern fields. The western coals are lower in heating value than the eastern coals. About 90 percent of the known deposits are located in four U.S. Geological Survey provinces: Eastern, Interior, Northern Great Plains, and Rocky Mountains (Figure 6). Table 4 shows the distribution of coal resources among these provinces.

TABLE 4. COAL RESOURCES IN U.S. GEOLOGICAL SURVEY PROVINCES*

Province	Identified	Undiscovered	Total
Eastern	276	45	321
Interior	277	259	536
Northern Great Plains	695	763	1458
Rocky Mountains	187	395	582
Other	146	181	327
Total	1581	1643	3224

Source: Averitt, 1973:137.

*Because available estimates are by state and USGS Provinces cross state boundaries the figures for these provinces are only approximate.

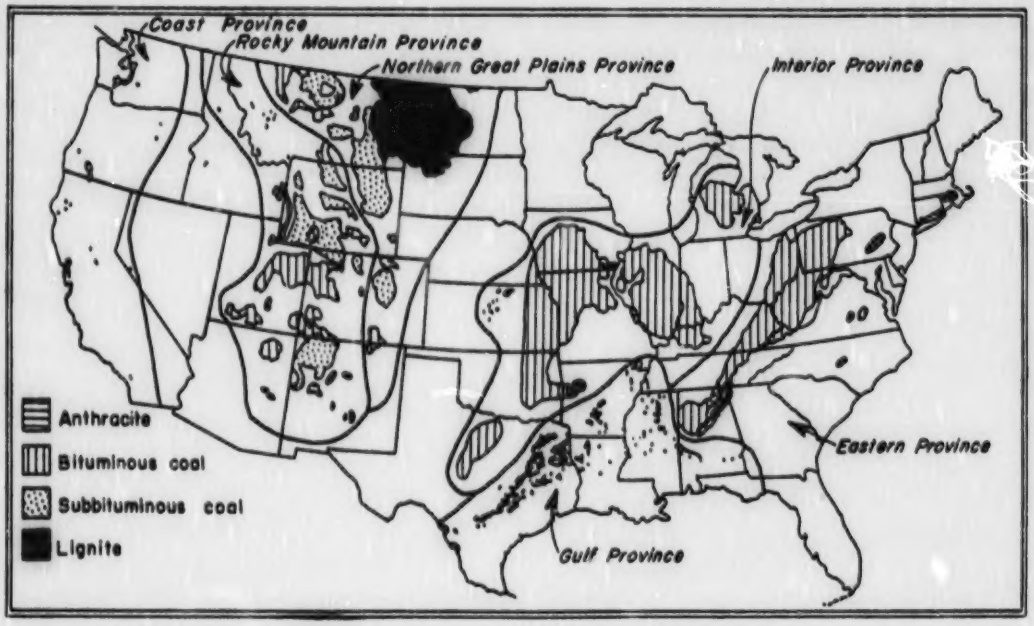

FIGURE 6. DISTRIBUTION OF UNITED STATES COAL RESOURCES

C. Tar Sands

Tar sands (alias bituminous sands, oil impregnated sandstone, etc.) are present in significant quantities in both the United States and Canada. Approximately one trillion barrels of oil in place

are contained in an area of Alberta, Canada some 200 miles north of Edmonton. Since 1967 a company known as Great Canadian Oil Sands, Limited, a subsidiary of Sun Oil Company, has been producing approximately 50,000 barrels per day of high quality synthetic crude from the oil sands.

The reason for the relative success of the Canadian oil sands operations is the nature of the oil sand deposits which exist there. Not only are the deposits gigantic, but they are easily accessible, possess homogeneous properties, and therefore are fairly easy to treat. On the other hand, U.S. deposits are almost miniscule by comparison, are largely inaccessible, and have properties which make extraction very difficult.

The only U.S. deposits which can seriously be considered to have any commercial potential are located in Utah. The in-place reserves of the five largest deposits total only 25 billion barrels and the breakdown is as follows:

Asphalt Ridge	1.1 billion barrels
P.R. Spring	4.5
Sunnyside	4.0
Circle Cliffs	1.3
Tar Sand Triangle	12.5

Because these U.S. deposits are relatively small and are not amenable to recovery by any currently known processes, it is unlikely that they will play any significant role in the future U.S. energy supply picture.

III. REVIEW OF PROCESSES

A. Oil Shale

Practically all processes designed to extract the hydrocarbon material (kerogen) from raw oil shale involve the application of heat. This heat energy causes the kerogen to thermally degrade, or pyrolyze, into a heavy hydrocarbon liquid syncrude. The conditions under which this pyrolysis reaction takes place can significantly affect the properties of the resulting oil product. Specifically, if the so-called "retorting" process requires the product oil to encounter excessively high temperature zones, some degree of thermal cracking may result, thus leading to the production of an upgraded product and a higher gas yield. Similarly, if the pyrolysis reaction takes place at a very low temperature, and therefore over a long period of time, noticeably greater concentrations of paraffinic compounds are likely to be present in the final oil product.

In addition to the slightly different products generated by the various retorting processes, each has associated with it a variety of environmental and operational advantages and disadvantages.

1. Gas Combustion Process

The Gas Combustion process has probably been the most thoroughly investigated retorting process to date. In this process 3 to 4-inch shale feed is placed in a vertical retort and a firefront is started in the bed. Combustion is maintained by the injection of air. As the firefront advances, it heats up the shale immediately in front of it, driving off the products of pyrolysis. These products are collected from the bottom of the retort.

This process can be modified to allow shale to be added and removed continuously. Raw oil shale feed is continuously fed to the retort at the top and withdrawn from the bottom. As the shale passes through the retort it encounters higher and higher temperatures until the majority of the kerogen is pyrolyzed to oil. This product oil is collected at the top of the retort while the hot shale passes downward into the combustion zone and the residual hydrocarbons and carbon are burned off to provide heat for the pyrolysis reaction.

2. TOSCO II Process

The retorting process which has probably received the most attention during the past few years is the TOSCO II process, developed by The Oil Shale Corporation (TOSCO). Unlike the Gas Combustion process, in which the heat-generating combustion process takes place within the retorting vessel, the TOSCO II technique employs indirect heating of the shale. The mechanism by which the heat of retorting is supplied is through the use of ceramic heat carriers. These heat carriers are 1/2-inch diameter balls heated in an external heater and then mixed with the raw shale in a retorting drum. The products of pyrolysis are collected from the drum and the spent shale and balls are sent to a collection device where the balls are separated and returned to the heater.

Because the heat transfer mechanism employed by the process is primarily solid-solid rather than gas-solid, the efficiency of the heating process is fairly low. In addition, due to the required transfer of large quantities of ceramic balls as well as shale solids, the problems inherent in solids material handling are increased. The primary offsetting advantages to these problems are the process' proven operability and limited gas handling problems.

3. *Paraho Process*

The Paraho process is capable of operating in essentially the same way as a Gas Combustion retort. Unlike the Gas Combustion retort, however, the Paraho retort is capable of being quickly modified to allow for the recycle of hot gas rather than internal combustion.

The hot gas recycle technique produces essentially the same type of high Btu gas and shale oil as the TOSCO II retort, the tradeoff between systems lying primarily in the solids-versus-gas handling problems. The TOSCO process requires the circulation of large quantities of solids (shale and ceramic balls), and in addition the shale feed must be of under 1/2-inch size. The Petrosix or Paraho (indirect heated mode) retort, on the other hand, involves the handling of large quantities of gases but can process shale feed up to 3 to 4 inches in diameter, thus minimizing crushing, handling, and disposal problems.

4. *In Situ Processes*

While many companies have investigated in situ production, both in bench scale and pilot plant operations, the only firm currently conducting actual field tests is Occidental Petroleum. Much of the theoretical work which led to the Occidental tests, however, was conducted at the Laramie Energy Research Center in Wyoming. In these tests, oil shale rock was packed in above-ground vessels and retorted in such a way as to simulate actual underground conditions.

Occidental Petroleum uses what is known as a *modified in situ* process, meaning that a cavity is first mined conventionally and the overlying shale formation is explosively expanded to fill the void. When done properly, the void space of the mine cavity is then distributed throughout the rubblized rock. The "chimney" created by rubblized rock (120 X 120 X 310 ft for Oxy's commercial operation) is then ignited at the top and a combustion front is allowed to move downward by continued injection of air from the top. Oil is produced and collected in a sump at the bottom of the retort and is subsequently pumped to the surface for further treatment.

B. Coal

The production of liquid products from coal requires the application of heat (up to 1500°F) and pressure (up to 5,000 psig) to accomplish a combination of hydrogenation and pyrolysis of the complex aromatic structures. Liquefaction processes by nature produce a range of products from gases (high hydrocarbons, H_2 CO, and CO_2) to heavy synthetic crudes. Crudes derived from coal generally have a lower hydrogen and higher nitrogen, sulfur, and aromatic content than conventional petroleum crudes. For this reason, synthetic crudes from coal require a certain degree of pretreatment before processing in a conventional petroleum refining facility. The aromatic content of synthetic crudes may provide an economic advantage over natural crudes in terms of the net value of the final products produced.

Coal liquefaction processes are of four general types: hydroliquefaction, solvent extraction, pyrolysis, and indirect liquefaction (liquids synthesis from H_2 and CO). *Hydroliquefaction* includes processes involving direct hydrogenation of coal through catalytic action. *Solvent extraction* implies processes which hydrogenate without catalysts through use of a hydrogen donor solvent. *Pyrolysis* processes drive off the volatile hydrocarbon gases and liquids by thermal cracking and carbonization. *Indirect liquefaction* processes catalytically synthesize low and middle distillate hydrocarbon compounds through polymerization of CO and H_2 products of coal gasification.

Coal feedstocks are more variable than petroleum feedstocks, and coal product markets are extremely susceptible to competition by easily transportable fluid fuels. Thus liquefaction research is not characterized by monolithic development toward a single "ultimate" liquefaction process, but rather, it is a continuing effort to broadly advance a series of processes specifically suited to limited ranges of feedstocks and markets. It is worthwhile to view individual unit operations of processes under development as potential elements of novel processes. A demand for these processes could arise in response to currently unforeseen supply/demand situations for which no specific existing process was suitable. Regional considerations such as water supply, size of coal sources, coal rank, composition, size of output capacity needs, and socio-economic factors may well dictate development of a number of different processes. Current program emphasis is on near term development of clean coal-based boiler fuel to supply existing oil-fired powerplants.

1. COED Process

The COED process, developed by the FMC Corporation under ERDA sponsorship, is a pyrolysis liquefaction process employing staged fluidized beds producing oil, char, and gas.

In the COED process, coal is crushed, dried and then heated to successively higher temperatures in a series of fluidized-bed reactors. In each fluidized bed, a fraction of the volatile matter of the coal is released. The temperature of each bed is selected to be just short of the maximum temperature to which the coal can be heated without agglomerating and defluidizing the bed. Typically, four stages operating at 600°F, 850°F, and 1500°F are involved. The number of stages and the operating temperatures vary with the agglomerating properties of the coal. Heat for the process is generated by burning char in the fourth stage and then using hot gases and the hot char from the fourth stage to heat the other vessels.

The volatile matter released from the coal in the pyrolysis reactors is condensed in a product recovery system. The pyrolysis oil product thus derived is filtered by a pressurized, rotary-drum, precoat filter to remove solids representing char fines which are carried through the cyclones of the fluidized-bed reactors.

Hydrotreating of the oil occurs in a fixed-bed catalytic reactor containing commercial nickel-molybdenum catalyst. Hydrotreating reactions remove sulfur, nitrogen and oxygen from the oil and can produce a 25-30° API synthetic crude oil product.

Yields based on Illinois No. 6 seam coal are: oil (19.3 percent), char (59.5 percent), gas (15.1 percent), and liquor (6.1 percent).

2. Hydrocarbonization Process

The conceptual design of a demonstration plant includes five processing areas:

- Coal preparation
- Hydrocarbonization
- Product cooling and liquids separation
- Gas processing
- Hydrogen generation.

Coal is sized and preheated prior to entering the reactor by entrainment in a stream of hot hydrogen.

Coal is injected directly into the fluid-bed reactor from the coal-feed vessel. The sole fluidizing medium is hydrogen. Product gas and oil exit the reactor at the top, passing through two cyclones to remove entrained ash and unreacted coal particles.

The hydrocarbonization process is essentially pyrolysis in a hydrogen atmosphere, producing to a great extent hydrogenated products. The exothermic heat of reaction between the hydrogen and coal maintains reactor temperature and is controlled as a reactor temperature parameter.

The reaction products pass forward from the external cyclone for subsequent cooling and separation. After removal of heavy and light oil products, hydrogen is removed cryogenically and is returned to the coal hydrocarbonization area.

LPG and SNG (high-Btu pipeline quality gas) are subsequently recovered from the reactor off-gas stream. Byproducts recovered are ammonia and sulfur.

Char from the hydrocarbonization area is gasified and the CO-rich gas shifted by steam saturation and catalysis to a 3:1 H_2/CO, ratio to produce additional process hydrogen.

3. H-Coal Process

The H-Coal process has been developed as a further application of the catalytic, ebullated-bed reactor technology employed to convert heavy oil residues into lighter fractions.

Design specifications call for a pilot plant to produce low-sulfur fuel oil, and synthetic crude suitable for refinery processing into gasoline, kerosene, diesel fuel, fuel oil and petrochemical feedstocks. Of the various categories of liquefaction processes, the H-Coal process would be termed hydroliquefaction.

Prepared coal is slurried with process-derived oil to which is added compressed, make-up hydrogen. The slurry and hydrogen are fed to preheaters at the base of the catalytic (Co/Mo) ebullated-bed reactor, along with recycled high-pressure gas that is similarly preheated. The catalyst in the reactor is suspended in the ebullated bed by the additional internal recycle-oil flow.

Reaction products pass overhead for subsequent liquid/gas separation. The light ends are removed as an overhead vapor product and sent to conventional recovery facilities such as absorption and low-temperature fractionation. Hydrogen gas is recycled to the reactor.

The liquid product, which is a slurry of oil, ash and unconverted coal, is flash-separated with the overhead going to atmospheric distillation for separation into light and heavy distillates. A portion of the bottoms liquid is partially clarified, in this case via a hydroclone, and the balance goes to vacuum distillation along with the concentrated slurry from the hydroclone. A solids-free heavy distillate is produced as the vacuum tower overhead; and a heavy residuum, containing essentially all the solids from the reaction section, is produced as the bottoms. The recycle oil for slurrying the coal can be a combination of partially clarified oil from the hydroclone with heavy distillate from both the atmospheric and vacuum towers. Since the solids content of the

slurry oil has an effect on the product distribution, it is beneficial to tailor its composition to obtain the most desirable product spectrum.

4. Solvent Refined Coal Process

The SRC process is a solvent extraction process producing low ash, low sulfur coal extract that is solid at ambient conditions. Further hydrogenation of the solvent refined coal yields a liquid synthetic crude. Hydrotreatment studies of SRC have not been extensively conducted to date.

In the SRC process, the coal is first dissolved under moderate hydrogen pressure (synthesis gas–CO and H_2–has been shown to effect solvation and may be a suitable substitute for H_2) in a heavy aromatic solvent derived from the process. The resulting coal solution is filtered to remove ash and a small amount of insoluble organic material and fractionated to recover the solvent. The main product from the process is a heavy organic material called Solvent Refined Coal which has a melting point of about 350°F and contains less than 0.1 percent ash and less than 0.8 percent sulfur. Its heating value is about 16,000 Btu per pound regardless of the quality of the coal feedstock. Smaller quantities of hydrocarbon gases and light distillate liquids are also produced. The solvent refining process removes all the inorganic sulfur and 60 to 70 percent of the organic sulfur in the coal. This organic sulfur is converted to H_2S by hydrogenation, then recovered as elemental sulfur from the hydrogen recovery and gas desulfurization unit.

5. Synthoil Process

The Synthoil process is a catalytic coal hydroliquefaction process originally developed by the Bureau of Mines.

The Synthoil process requires that ground dried coal be mixed with a recycled portion of its own product oil. The resultant slurry, along with recycled hydrogen and makeup hydrogen is preheated and conveyed through the fixed bed catalytic reactor. The flow of hydrogen through both the preheater and the reactor is in the turbulent regime. The combined effect of hydrogen, turbulence, and catalyst liquefies and desulfurizes the coal.

The reactor is packed with a commercially available catalyst (cobalt-molybdate on silica-activated alumina) and operating conditions are 840°F and 2,000-4,000 psig.

Effluent gases are separated from the extract in the high-pressure receiver and the hydrogen rich gas is recycled after the removal of H_2S, NH_3, H_2O and gaseous hydrocarbon. Product slurry oil pressure is reduced in passing to a low-pressure receiver and is then filtered (or centrifuged) to remove the unreacted solids consisting of mineral matter and refractory coal substance. Part of the nonpolluting fuel oil is recycled as slurry oil. The product oil flows freely at room temperature and has less than 0.3 percent sulfur content.

The solids from the solids separator go to a pyrolyzer, which yields an additional quantity of product oil and a carbonaceous residue consisting mostly of mineral matter. This residue together with the gaseous hydrocarbons from the gas purification system is fed to a gasifier to prepare makeup hydrogen for the process.

Kentucky Coal, Pittsburgh Seam Coal, Indiana No. 5 Seam Coal, Middle Kentucky Kittanning (Ohio) Coal and a Wyoming coal have been processed by this method, and in all cases a product was obtained which contained less than 0.39 percent sulfur.

6. Fischer-Tropsch Process

The Fischer-Tropsch process is a simple and proven process to produce synthetic hydrocarbons and chemicals from hydrogen and carbon monoxide. The synthesis gas can be obtained by gasification of coal and refining of natural gas. The process catalytically combines CO and H_2 through polymerization reactions to produce straight long-chain hydrocarbons and alcohols. Products, after refining, include gasoline, fuel oil, SNG, and PG.

As only one commercial plant, *SASOL* in South Africa, is currently in operation to produce liquid hydrocarbons from coal-derived synthesis gas via Fischer-Tropsch Synthesis, the following description is for that plant.

Coal is gasified in a battery of 13 Lurgi gasifiers to produce a gas consisting essentially of carbon monoxide and hydrogen. The gas stream from the gasifiers is quenched to remove tar and oil and purified. The purified synthesis gas stream is partitioned and a part of the gas is passed through a fixed-bed catalytic reactor (Arge synthesis). Synthesis occurs under conditions of 430°F and 360 psi. The products of the Arge synthesis are straight-chain, high-boiling hydrocarbons, with some medium-boiling oils, diesel oil, LPG, and oxygenated compounds such as alcohols.

The portion of the synthesis gas which was not sent to the Arge unit goes to the Synthol plant (Kellogg synthesis) which is a fluidized-bed catalytic (iron) reactor. Operating conditions are 600° to 625°F and 333 psi.

The raw products from the synthesis require certain treatment and then final purification to make the specification products. From the gas phase, valuable hydrocarbon and chemical products are scrubbed out and recovered. The oil phase is treated catalytically to remove dissolved oxygenates and then distilled into gasoline and fuel oil fractions. The remaining liquor is distilled and fractionated to produce chemical products. Heavy alcohols to pentanol are also recovered.

C. Tar Sands

There are no significant existing or anticipated processes for the recovery of United States' tar sand hydrocarbon materials because of (a) the relatively small quantities of tar sands in the U.S., (b) the fundamentally different nature of U.S. tar sands agglomerate which requires disproportionate expenditure of energy to extract the material and (c) the fact that U.S. tar sand is some 10 to 20 feet below the surface in thin veins as opposed to the Canadian reserves which lie directly on the surface.

IV. SYNTHETIC CRUDE PRODUCTS

A. Petroleum Crude

Some of the more important properties of a petroleum crude oil are shown in Table 5 for comparison with properties of the various syncrudes given subsequently in this section. It cannot be said that this is a typical crude because properties of petroleum crudes vary extensively. For example, gravities in API units can vary from 13 to 60 deg and sulfur content from less than 0.10 weight percent to 4 percent or more. Nitrogen contents of petroleum have been found to range between <0.01 to around 0.7 percent.

TABLE 5. GENERAL CHARACTERISTICS OF PETROLEUM CRUDE FROM BAGLEY FIELD, NEW MEXICO

Gravity, °API	46.0
Carbon residue, %	0.1
Pour point, °F	below 5
Sulfur, wt %	0.34
Nitrogen, wt %	0.008
Distillation range, °F	
IBP	104
Final BP	790
Residue, %	7.6

B. Oil Shale

In general, raw shale oils derived from Green River oil shale possess markedly different characteristics than conventional crude petroleum. These differences include:

- High olefin content due to pyrolytic processing,
- High nitrogen and oxygen content derived from the shale organic material and
- High pour points and viscosities.

The specific values of each of the above properties vary somewhat, depending on the particular retorting process used, the temperature and pressure conditions existing during retorting, the grade of the shale being processed, and the concentration of various mineral constituents in the raw shale. In addition to the retorting variables, one of the most important factors in determining the quality of the final oil product is the efficiency and method of collecting the hydrocarbon vapors and condensing them into oil. Because the oil product is composed of hydrocarbon materials having a full range of boiling points, the temperature and pressure of the collection apparatus will determine how many of the materials end up in the liquid product and how many are to be burned as process fuel gas. Differences in collection temperatures of 50°F could conceivably result in liquid products having 3 to 5 deg API gravity differences.

TABLE 6. PROPERTIES OF RAW OIL SHALE FROM USBM GAS COMBUSTION RETORT

Oil collected, vol % of Fischer Assay	82
Gravity, °API	21
Ramsbottom carbon, wt %	1.4
Pour point, °F	85
Sulfur content, wt %	0.67
Nitrogen content, wt %	2.13
Vacuum Distillation (ASTM D-1160, corrected to 760 mm Hg)	
IBP	369°F
2%	399
5	446
10	499
20	590
30	670
40	744
50	812
60	870
70	918
80	984
90	1065
Recovery, %	91

Keeping the above comments in mind, and recognizing that the properties of oil products from a pilot unit are not necessarily the same as those to be expected from a commercial facility, one may now examine the product properties of the major retorting processes and make some fairly generalized observations.

1. Gas Combustion Process

The most comprehensive collection of data regarding the Gas Combustion retorting process was that compiled by the U.S. Bureau of Mines in Bulletin 635, published in 1966. A review of the data shows that the average properties of the raw shale oil produced were as shown in Table 6.

Because the Gas Combustion process involves the combustion of material in the retort vessel itself, it is likely that a substantial quantity of light hydrocarbons produced by the pyrolysis reaction are also consumed. This is demonstrated by the fact the oil yield averaged only 82 volume percent of Fischer Assay, whereas indirect heated type retorts generally yield in excess of 100 volume percent. A comparison of these product properties with those of some indirectly heated retorts also shows the Gas Combustion oil to be slightly heavier, thus indicating that some quantity of light ends is lacking in the oil.

2. *TOSCO II Process*

The source of most data regarding the TOSCO II process is from representatives of the Oil Shale Corporation. According to their report, the crude shale oil produced by the TOSCO II process would have the properties shown in Table 7. It was claimed that the process recovered substantially 100 percent of the recoverable hydrocarbon in the oil shale as determined by the Fischer Assay technique.

TABLE 7. PROPERTIES OF CRUDE SHALE OIL FROM TOSCO II RETORT

Component	Vol %	°API	Sulfur wt %	Nitrogen wt %
C_5-400°F	17	51	0.7	0.4
400-950°F	60	20	0.8	2.0
950°F +	23	6.5	0.7	2.9
Total	100	21	0.7	1.9

TABLE 8. PROPERTIES OF HYDROTREATED SHALE OIL FROM TOSCO II RETORT

Component	Vol %	°API	Nitrogen ppm
C_5-400°F	43	50	1
400-650°F	34	35	800
650-EP	23	30	1200
Total	100	40	

TABLE 9. PROPOSED PROPERTIES OF PHASE I UPGRADED SHALE OIL FROM TRACT C-a PROJECT

Gravity, °API	28.6
Max true vapor pressure, psia	8.0
Max viscosity, SSU @ 30°F	800
Max pour point, °F	30

TABLE 10. PROPOSED PROPERTIES OF PHASE II UPGRADED SHALE OIL FROM TRACT C-a PROJECT

Gravity, °API	45.2
Reid vapor pressure, psia	5
Sulfur, ppm	10
Nitrogen, ppm	510
Arsenic, ppm	8

The pour point of the oil product was initially 80° to 85°F, but TOSCO has a patented (U.S. Patent No. 3,284,336) process by which this pour point may be lowered to 30°F or less. This process reportedly involves heating the heavy portion of the oil to 700° to 750°F for about 30 minutes and then recombining this material with the cooler light ends. Evidently, the heat treating step generates substances which can serve as effective pour point depressants.

The TOSCO report also describes an upgrading scheme by which the crude shale oil can be converted to a high quality synthetic crude. This process would involve a delayed coking step followed by naphtha and gas oil hydrotreaters. The upgraded product would likely have the properties shown in Table 8.

The recently released *Detailed Development Plan for Tract C-a* (DDP), published by Standard of Indiana and Gulf Oil, describes a raw oil recovery system and upgrading scheme by which the shale oil may be converted into a pipelineable product having the properties shown in Table 9.

Rather than using a series of hydrotreaters, the Amoco-Gulf plan involves the initial fractionation of the shale oil followed by a thermal cracking operation. The DDP also describes a more comprehensive upgrading scheme for the second phase of their operation. This process involves an initial fractionation step followed by delayed coking and two hydrotreating trains. This process is similar to that described in the TOSCO report. The properties of the product oil from this process are shown in Table 10.

3. *Paraho Process*

As described in the preceding section of this report, the Paraho retort now in use at the Anvil Points facility is capable of operating in both the direct and indirect heated mode. To date, however, the only data available are in relation to the direct, or internal combustion, mode of operation. Information provided in the report entitled "The Production and Refining of Crude Shale Oil into Military Fuels" by Applied Systems Corporation shows that the raw shale oil produced by the Paraho retort had the properties shown in Table 11.

TABLE 11. PARAHO RETORT CRUDE SHALE OIL

Physical Properties	
Gravity, °API	19.3
Spec gravity (60/60)	0.9383
Pour point, °F	85.0
Viscosity (cs @ 210°F)	6.38
Viscosity (cs @ 140°F)	20.15
Tot acid no. mg KOH/gm	1.969
BS&W, vol %	0.4
Asphaltenes, wt %	0.819
Rams carbon, wt %	1.383
Ultimate Analysis, wt %	
Carbon	84.90
Hydrogen	11.50
Oxygen	1.40
Nitrogen	2.19
Sulfur	0.61
Selected Metal Concentration, ppm	
Arsenic	19.6
Nickel	2.5
Iron	71.2
Vanadium	0.37
D285 Hempel Distillation of Whole Crude Shale Oil, vol %: (IBP-238°F)	
270°F = 0.1	
300°F = 0.3	
340°F = 0.7	
400°F = 2.0	
450°F = 5.1	
500°F = 11.8	
500° + residue = 87.8	
Distillation loss = 0.4	

It is highly unlikely that the trace metals shown in Table 11 would be present in finished gasoline since they would be removed by catalytic reactions used in conventional petroleum refining processes. Virtually all the arsenic in the Paraho analysis was contained in the residual sample (>843°F) and thus would not be carried beyond the initial refining distillation phase.

The raw shale oil was subsequently refined in the Gary Western refinery at Gilsonite, Colorado. The process involved the use of a delayed coker and several trains of hydrotreaters and desulfurizer units. Rather than a blended synthetic crude product, an entire range of end products was included in the product slate, and thus some catalytic cracking and reforming operations were also involved. The products produced were:

- Combat gasoline
- JP-4
- JP-5/Jet A
- Diesel fuel marine/No. 2 diesel fuel
- Heavy fuel oil.

According to recently released reports on the refining operation, the products did not meet all the specifications established by the military, but this was due to inadequate processing rather than any major deficiencies in the oil shale feed itself.

4. *Other Aboveground Processes*

Because of the proprietary nature of the work being done by Superior Oil Company on their circular grate retort, the detailed analysis of the product oil is not available. Considering the conditions which would be expected in that type of retort, however, the properties are likely to be very similar to those of oil produced in any other indirectly heated retort such as the Petrosix or TOSCO II. Due to the fairly low heating rate which may be expected, the paraffin content of the oil may be slightly greater than that from other processes. It must also be taken into account that the oil shale feed for the Superior process is from the northern outcrop area of the basin and this may significantly affect the final oil properties.

TABLE 12. PROPERTIES OF SHALE OIL FROM UNION ROCK PUMP RETORT

Gravity, °API	22.7
Carbon, wt %	84.8
Hydrogen, wt %	11.61
Nitrogen, wt %	1.74
Sulfur, wt %	0.81
Oxygen, wt %	0.90
Ash, ppm	50
Pour point, °F	60
Viscosity, sus @ 100°F	98.2
Distillation, Modified Engler	
IBP	139°F
10%	400
50%	731
90%	960
EP	1077

Likewise, no information is immediately available regarding the properties of oil from the Lurgi-Ruhrgas process. However, one would naturally expect the values to be similar to those of oil from the Petrosix or TOSCO II processes.

Recent publications by Union Oil Company give a very brief description of the product oil expected from their "rock pump" retort. These properties are shown in Table 12.

5. *In Situ Processes*

As discussed in Section III of this report, the most advanced in situ recovery technique is that of Occidental Petroleum. Like the other proprietary processes for aboveground extraction, very little detailed information is available on the properties of the product from the Oxy process. From a totally theoretical point of view, however, one would not expect the final product to be much different than that produced by the Gas Combustion retort. The retorting process is essentially the same with the only real difference being the vessel in which the process takes place. For the aboveground processes the container is a steel drum whereas for the in situ process the container is a solid wall of unbroken oil shale. Due to the dynamics of the large-scale in situ operation, however, it would be reasonable to expect a significant change in product properties from the beginning to the end of the retorting process.

TABLE 13. PRODUCT YIELD DISTRIBUTION FOR COED PROCESS (PER TON)

Coal	Syncrude Bbl	Gas Scf	Char lb
Utah	1.3	9,500	1,200
Illinois	1.1	9,000	1,200
Colorado	1.0	8,000	1,100
W. Kentucky	0.9	6,000	1,250
Wyoming	0.7	18,000	1,000
N. Dakota (Lignite)	0.4	12,000	1,400

C. Coal

1. *COED Process*

The COED facility has operated on a variety of coals, ranging from North Dakota lignite to West Virginia high-volatile A-bituminous. The final product yields from some of these feeds are shown in Table 13. The properties of the hydrotreated synthetic crude from Illinois and Utah coal are shown in Table 14. Additional data regarding the synthetic crude properties are shown in Table 15.

TABLE 14. PROPERTIES OF HYDROTREATED SYNCRUDE FROM COED PROCESS

Property	Illinois	Utah
Composition, vol %:		
Paraffins	10.4	23.7
Naphthenes	41.4	42.2
Aromatics	48.2	34.1
Distillation, °F:		
Initial boiling point	108	260
50% distilled	465	562
End point	746 (98%)	868 (95%)
Fractionation, wt %:		
IBP-180°F	2.5	0.0
180-390°	30.2	5.0
390-525°	26.7	35.0
525-650°	24.3	30.0
650-end point	16.3	30.0

TABLE 15. SYNCRUDE PROPERTIES FROM COED PROCESS

Test	Result
Flash point, CC °F	46
Pour point, °F	<-36
Water and sediment, vol %	Trace
Ash, wt %	<0.005
ASTM Distillation, °F	
IBP	191
10%	273
50%	518
90%	684
95%	720
Viscosity, at 100°F	3.4
API Gravity	27.2

2. *Hydrocarbonization*

Very little information is publically available regarding the properties of product from this process as it has to date been developed privately. Some data have been released, however. These data are from a unit operated on low sulfur subbituminous coal from the Lake De Smet region of Wyoming. The product properties are shown in Table 16. Also shown in the table are data for Pittsburgh No. 8 coal to be expected using the De Smet data as a base.

3. *H-Coal Process*

The properties of product from the H-Coal process are shown in Tables 17 and 18.

4. *Solvent-Refined Coal Process*

The typical properties of solvent-refined coal are shown in Table 19. The refined coal has a

TABLE 16. PRODUCT PROPERTIES FROM HYDROCARBONIZATION PROCESS

Product Properties	Lake De Smet	Pittsburgh No. 8
Yields, lb/100 lb MAF Coal		
Liquids	21.25	32.1
Hydrocarbon gas	13.20	18.0
Water	11.41	5.0
CO, CO_2, NH_3, H_2S	13.28	5.3
Char	43.02	43.0
Hydrogen uptake	−2.17	−3.4
	100.0	100.0
Proximate Analysis (as received)		
Moisture	28.5	4.8
Volatiles	30.0	35.1
Fixed carbon	33.3	50.3
Ash	7.6	7.5
Total sulfur	0.6	2.3
	100.0	100.0
Gross Heating Value, Btu/lb	10,000	10,000

TABLE 17. PROPERTIES OF PRODUCTS FROM H-COAL PROCESS

Product Properties	Illinois Coal		Wyodak Coal
	Synthetic Crude*	Low-Sulfur Fuel Oil*	Synthetic Crude*
Normalized Product Distribution			
C_1-C_3 hydrocarbons	10.7	5.4	10.2
C_4-400°F distillate	17.2	12.1	26.1
400-650°F distillate	28.2	19.3	19.8
650-975°F distillate	18.6	17.3	6.5
975°F + residual oil	10.0	29.5	11.1
Unreacted ash-free coal	5.2	6.8	9.8
$H_2O, NH_3, H_2S, CO, CO_2$	15.0	12.8	22.7
Total (100.0 + H_2 Reacted)	104.9	103.2	106.2
Conversion, %	94.8	93.2	90.2
Hydrogen consumption, SCF/ton	18,600	12,200	23,600
*Desired Product.			

TABLE 18. PRODUCT INSPECTIONS OF C_4 + LIQUID FROM H-COAL PROCESS

Product Properties	Illinois Coal		Wyodak Coal
	Synthetic Crude*	Low-Sulfur Fuel Oil*	Synthetic Crude*
Gravity, °API	15.0	4.4	26.8
Hydrogen, wt %	9.48	8.43	10.54
Sulfur, wt %	0.19	0.43	0.16
Nitrogen, wt %	0.68	1.05	0.64
*Desired Product.			

TABLE 19. TYPICAL PROPERTIES OF SOLVENT-REFINED COAL

Properties	Feed Coal*	Solvent Refined Coal
Carbon	70.7	88.5
Hydrogen	4.7	5.1
Nitrogen	1.1	1.8
Sulfur	3.4	0.8
Oxygen	10.0	3.7
Ash	7.1	0.1
Moisture	3.0	0.0
	100.0	100.0
*Western Kentucky Bituminous.		

heating value of about 16,000 Btu/lb and is fairly uniform in analysis regardless of the coal feed used.

The raw refined coal is usually solid at ambient conditions but may be further hydrotreated, hydrocracked, or coked to produce more valuable liquids.

5. *Synthoil Process*

The most recent data regarding the products of the Synthoil process were presented by representatives of Pittsburgh Energy Research Center at the "Clean Fuels from Coal" Symposium in 1975. These data are shown in Tables 20 and 21.

6. *Fischer-Tropsch Process*

Table 22 shows the products obtained by the Fischer-Tropsch process with the Arge fixed bed system as operated at the SASOL facility. This system is operated for production of light

TABLE 20. PROPERTIES OF PRODUCT FROM SYNTHOIL PROCESS USING KENTUCKY COAL FEED

Products from Reactor			
	4,000 psi		2,000 psi
Preheater outlet temperature, °C	450	430	430
S in product oil, wt %	0.2	0.45	0.5-0.7
Ash in product oil, wt %	0.1-0.2	0.75	1.3-2.9
Viscosity of product oil, SSF	[1] 26-440	[2] 10-30	[3] 14-98
Specific gravity of product oil 60°F/60°F	1.020-1.082	1.034-1.094	1.060-1.148
Calorific value of product oil Btu/lb	17,400	17,800	16,640
Yield of product oil, bbl/ton of coal (as received)	3.3	3.2	3.0
Consumption of H_2, scf/bbl of product oil (1 at 77°F) (2 at 180°F)	4,375	4,170	3,450
Products Following Centrifugation			
Pressure, psi	4,000 psi		2,000 psi
Preheater temperature, °C	450	430	430
Residues, wt % of whole product	11.7	12.1	12.1
S in residues, wt %	4.6	5.2	4.9
Solvent Analysis of Residues, wt %			
Ash	52.8	53.0	55.3
Organic benzene insolubles	14.9	14.1	17.5
Asphaltenes	3.1	5.6	6.5
Oil	29.2	27.3	20.7
Centrifuged liquids, wt % of whole product	88.3	87.9	87.9
S in centrifuged liquids, wt %	0.2	0.45	0.6
Solvent Analysis of Centrifuged Liquids, wt %			
Ash	0.1	0.75	2.1
Organic benzene insolubles	0.8	0.9	4.4
Asphaltenes	10.8	18.7	27.6
Oil	88.3	79.65	65.9

TABLE 21. PROPERTIES OF PRODUCT FROM SYNTHOIL PROCESS USING WEST VIRGINIA COAL FEED

Products from Reactor		
	4,000 psi	2,000 psi
Preheater outlet temperature, °C	450	450
S in product oil, wt %	0.4	0.6
Ash in product oil, wt %	0.5	1.6
Viscosity of product oil, SSF[1]	18-40	56-585
Specific gravity of product oil, 60°F/60°F	1.056-1.093	1.129-1.174
Calorific value of product oil, Btu/lb	17,000	16,700
Yield of product oil, bbl/ton of coal (as received) (1 at 180°F)	3.4	3.2
Products Following Centrifugation		
Pressure, psi	4,000 psi	2,000 psi
Preheater temperature, °C	450	450
Residues, wt % of whole product	8.2	9.1
S in residues, wt %	4.9	5.8
Solvent Analysis of Residues, wt %		
Ash	41.7	34.6
Organic benzene insolubles	22.9	26.0
Asphaltenes	6.4	11.2
Oil	29.0	28.2
Centrifuged liquids, wt % of whole product	91.8	90.9
S in centrifuged liquids, wt %	0.4	0.6
Solvent Analysis of Centrifuged Liquids, wt %		
Ash	0.4	1.6
Organic benzene insolubles	2.4	13.0
Asphaltenes	21.3	30.1
Oil	75.9	55.3

TABLE 22. PROPERTIES OF LIQUID PRODUCTS FROM SASOL FACILITY

Selectivities %	Arge	Synthol	Pilot Plant		
CH_4	5.0	10.0	30	50	70
C_2H_4	0.2	4.0			
			15	17	12
C_2H_6	2.4	6.0			
C_3H_6	2.0	12.0			
			15	11	6
C_3H_8	2.8	2.0			
C_4H_8	3.0	8.0			
			16	13	6
C_4H_{10}	2.2	1.0			
Petrol C_5-C_{12}	22.5	39.0	20	7	
Diesel C_{13}-C_{18}	15.0	5.0	1.5	0.5	
					6
Heavy oil C_{19}-C_{21}	6.0	1 0			
and C_{22}-C_{30}	17.0	3.0	1.5	0.5	
wax C_{31}+	18.0	2.0			
NAC	3.5	6.0	1	1	0.2
Acids	0.4	1.0	0.05	0.05	0.05
	100.0	100.0	100.0	100.0	100.0

TABLE 23. PROPERTIES OF LIQUID PRODUCTS FROM SASOL FACILITY

Liquid Products	Arge		Synthol	
	C_5-C_{12}	C_{13}-C_{18}	C_5-C_{10}	C_{11}-C_{14}
% Paraffins	53	65	13	15
% Olefins	40	28	70	60
% Aromatics	0	0	5	15
% Alcohols	6	6	6	5
% Carbonyls	1	1	6	5
% n Paraffin	95	93	55	60

hydrocarbons and motor fuels with some desirability for light olefins such as ethylene and propylene. By changing conditions, it is possible that the fixed bed plant could be made to produce the same slate as the Synthoil plant. Table 23 gives a further breakdown of the properties.

D. Tar Sands

Although it has been stated earlier that the production of oil from U.S. tar sands deposits will have little or no bearing on the future U.S. energy supply picture, it should be emphasized that extremely high quality material can and is being produced from Canadian tar sands deposits. In its raw state, bitumen from the tar sands is a much less desirable material than raw shale oil from any available retorting process. The properties of raw Athabasca bitumen are shown in Table 24. However, with proper treatment, this bitumen may be refined into an exceptionally good refinery feedstock. The typical properties of this synthetic crude oil are shown in Table 25. To demonstrate the value of this material, Table 26 lists the refiners who consistently purchase quantities of synthetic crude from the Great Canadian Oil Sands facility in Alberta.

TABLE 24. PROPERTIES OF RAW BITUMEN FROM ATHABASCA TAR SANDS

Gravity, °API	7.8
Viscosity, SUS @ 100°F	35,100
Carbon, wt %	83.2
Hydrogen, wt %	10.4
Oxygen, wt %	0.94
Nitrogen, wt %	0.36
Sulfur, wt %	4.2
Distillation	
IBP	505°F
5%	544
10%	610
30%	795
50%	981
EP	1030

TABLE 25. PROPERTIES OF SYNTHETIC CRUDE PRODUCED FROM ATHABASCA BITUMEN (DATA FROM GCOS FACILITY)

Gravity, °API	38.3
Carbon, wt %	86.3
Hydrogen, wt %	13.4
Nitrogen, wt %	0.02
Sulfur, wt %	0.03
Distillation	
IBP	162°F
5%	221
10%	254
30%	408
50%	507
90%	615
EP	715

TABLE 26. REFINERS PURCHASING QUANTITIES OF SYNTHETIC CRUDE OIL FROM GCOS

Refiner	Location
Northwestern Refining Co.	St. Paul Park, Minnesota
Shell Canada	St. Boniface, Manitoba
	Corunna, Ontario
Sun Oil, Ltd.	Sarnia, Ontario
	Toledo, Ohio

V. TECHNOLOGY PROJECTIONS

A. Refining Industry

The technology of today has been a continuously evolving process over the last 100 years in which gradual steps have been taken. The need for new processes has been a continual but not excessively demanding one, such that evolutionary progress and development was adequate. The economic requirements have been such that compatibility with existing hardware and facilities prevented radical growth or revision. The product specification demand has also been such that growth and development have been gradual. The quality of crude has been premium in most cases, and supply permitted selection of crude types to allow blending to meet process and product requirements. This systematic growth has resulted in a refining and processing industry capable of producing the required fuels for current automotive requirements.

In recent years, as the requirement has grown for specific products with more demanding specifications and the supply of premium domestic crude has dwindled, new technology has been developed to "reshape" the chemical nature of the crude regardless of its quality and source so that the desired product type and quality are obtained. These processes of cracking, reforming and hydrotreating when enhanced by long-practiced blending have served the fuels and chemicals market well.

As a result, the petroleum industry has developed processes to meet *product requirements*. Some of these processes are quite sophisticated and require very specific, carefully-controlled feedstocks. Deviation from the quality specifications of the feedstocks can result in serious degradation of the process or the catalysts used, or, in some cases, destructive explosions. Therefore, pretreatment of crudes and feedstocks is routinely performed to bring those materials into line before they are introduced to the refining process. One such commonly used pretreatment is hydrotreating. This process is applied at various points in the refining procedure, depending on the quality of the feedstock, the required product quality, and the process involved. Some of the effects of hydrotreating are the removal of elements such as oxygen, nitrogen and sulfur, the reduction of olefin content, the saturation of some aromatics, and the improvement of long-term stability.

Hydrotreating, in general, is a very powerful technique to "clean-up" low quality, marginal crudes and feedstocks. However, it does increase the cost of processing, with the more "contaminated" materials requiring more extensive and successive hydrotreating steps, thus further increasing costs. With these points in mind, it is obvious why the petroleum industry seeks out and processes high quality crudes in preference to those which would require heavy pretreatment and cleanup.

It is reasonable to expect further advances in processing technology over the next 25 years which will make new and improved methods available. However, the overall objectives of the refining industry can be met now with today's technology, and future requirements are not expected to be drastically different from today. The major areas of improvement in technology will probably be in higher efficiencies, better yields, better energy utilization and conservation, and higher production.

Synthetic crudes are, in effect, among the worst case examples of marginal petroleum crudes. These marginal crudes require, in many instances, extensive cleanup just to make them into reasonably stable and transportable materials. The shale oil produced from retorting contains olefins to

such an extent that the oil is unstable. The high density, high viscosity, and high pour point clearly demand significant supplemental processing such as hydrotreating to yield products of quality for transport and further refining or consumption. Upon receipt of such feedstocks, a contemporary refinery can preprocess the material to bring it within the acceptable specifications for that refinery. However, this extensive hydrotreating and processing only further increases the cost of the final products. As a result, syncrudes will have a severe handicap in competing with conventional crudes as refinery feedstocks.

This conclusion can be drawn for all syncrudes, regardless of source. Not only are the production processes new and expensive, but their future development will depend upon well-defined governmental energy policies. Industry and investors are less than eager to sink large sums of capital into programs which have uncertain, if not bleak, chances of financial success. As a direct consequence, only limited quantities of unconventional crudes are expected to be found on the crude market before 1990.

TABLE 27. ESTIMATED DAILY VOLUMES OF HYDROCARBON TYPE CRUDES MMBBLS/DAY EACH SOURCE

By The Year	Tar Sand	Oil Shale	Coal	Petroleum
1985	–	0.15-0.25	0.05	21.9
1990	0.01	0.3-0.75	0.2	23.3
2000	0.02	1.0-2.0	0.3-0.5	25.5

During 1990-2000, increasing supplies of syncrudes are anticipated but the total is still not expected to be of major significance. Table 27 gives an *optimistic* estimate of the daily volumes of synthetic crudes produced.

Even though only a small percentage of the total may come from synthetic sources, a still smaller percentage will be processed into gasoline. More likely, these syncrudes will be minimally processed to provide heating fuels with easier-to-attain specifications (and less expensive) thus relieving demands on petroleum crude supplies which can be processed more easily and at less cost.

In a minimum processing case for syncrudes, some desirable products are recoverable, such as light gases and naphthas. These materials will readily find their way into appropriate markets. Fortunately, these low-boilers are the least expensive to hydrotreat and process and are welcomed by the refiner. The higher boiling materials will supply the furnace oil market where impurities can be better tolerated and controlled.

Experts in the refining industry are currently in unanimous agreement that the influx of syncrudes *will have no effect on the composition of future gasoline*. The supply is not expected to be significant; the use is not expected to be for refined products, and that which is refined into gasoline *will totally lose its identity* in the refining process and in blending with streams refined from petroleum crudes.

B. Automotive Industry

The consensus within the refining industry regarding gasoline compositions and performance through the end of the 20th century is that (a) the industry can and will supply gasoline at any performance level required by dominant gasoline-powered internal combustion engines, (b) the cost of this gasoline will fluctuate (and rise) in response to recognized factors, and will be tolerated by the public up to a level of two or three times today's prices, and (c) syncrude materials will have little, if any, impact on gasoline quality or composition since the projected quantities from coal or shale will be minute in comparison with petroleum crude throughout.

The principal criteria for customer satisfaction and consequent gasoline demand during the next several decades will continue to be fuel performance and vehicle driveability. The projected quantities and distributions for these several engine types are dependent upon the rate of development of

less conventional automotive powerplants such as gas turbine, (small) diesel, and Stirling. Each of these, in turn, will be highly dependent upon the nature of vehicle emissions regulations that may become effective during the 1976-1980 time frame. Status of such regulations may be described as being in intermediate-to-advanced stages of finalization within Congress at this time with promulgation possible by 1978. Of the several components, by far the most pertinent and critical to new engine development will be the oxides of nitrogen (NO_x) standards for light-duty vehicles (currently 6000 lb GVW or less, which may be raised to 8500 GVW for light-duty trucks). This is the largest single production category as regards personal and small commercial vehicles. While there is some disagreement as to the *exact* value, promulgation of a NO_x standard above (roughly) 0.93 g/km will dramatically *increase* incentive to develop small diesel engines for light-duty transport vehicles. This would result in a correspondingly increased demand upon the middle distillate fraction of the refined hydrocarbon product. The conventional gasoline engine is nevertheless expected to constitute the dominant percentage of this category through 2000 A.D. Table 28 summarizes one such projection for the several engine types in the light-duty vehicle category with the noted assumptions.

TABLE 28. PROJECTED DISTRIBUTION OF U.S. LIGHT-DUTY AUTOMOTIVE MARKET

Type	1975	1980	1985	1990	1995	2000
Spark Ignition	99	98	90	85	75	60
Diesel	1	2	10	14	20	30
Stirling	0	0	0	1	5	10
Gas Turbine	0	0	0	0	0	0

Assumptions:
(1) NO_x Std >0.93 g/km; other stds. become increasingly stringent.
(2) No dramatic economic advantages of light-duty diesel over SI.
(3) Gas turbine remains uneconomical for light-duty vehicles.
(4) Stirling proves practicable, but requires long-term R&D.

Each of these engine types will be discussed in the subsequent subsections.

1. *Spark Ignition Engine*

It has already been stated that this engine is expected to continue to dominate the light-duty vehicle field for the balance of this century. This engine will probably require gasoline representative of requirements for the most recent production engines.

The effect of the several approaches to emissions control for the spark ignition engine will be dependent upon any "technological breakthroughs" (e.g., lean burn techniques, stratified charge) which serve to displace the catalytic converter. Barring breakthroughs in either converter or anti-knock technology, unleaded gasoline will become increasingly abundant as attrition reduces the ranks of vehicle systems compatible with leaded gasoline.

Two other engine-related factors could conceivably affect gasoline front-end volatility. These factors would be (a) promulgation of increasingly restrictive evaporative emissions standards, and (b) more widespread use of fuel injection technology. The latter is highly dependent upon the individual fuel injection design, some configurations being considerably more fuel-sensitive than others.

2. *Compression Ignition Engine*

The diesel engine's potential for light-duty vehicle application will, as discussed previously, be strongly affected by the pending decision on NO_x standards. Projections for the diesel's expansion in this area would indicate a linear growth of almost 1 percent per year through 2000 A.D. As acceptance increases, and diesel fuel presumably becomes more widely available, this

rate might conceivably double, especially if the small diesel proves to have economic advantages over the spark ignition engine (e.g., maintenance, improved fuel economy).

3. Gas Turbine Engine

Few advocates of the gas turbine automotive powerplant forecast extensive automotive use of this engine before 1985. Initial mass production–if manufacturing, maintenance and fuel economy problems can be overcome–will undoubtedly be composed of heavy-duty trucking engines with light-duty private vehicle marketing trailing by a few years. The gas turbine can–but probably will not–operate on gasoline. Conventional middle distillates and methanol seem far more likely at this point. Sulfur and metals content for gas turbine fuels, regardless of class, will be critical due to inherent sensitivity to turbine blade erosion and other corrosion-sensitive characteristics known for this powerplant.

The future for the automotive gas turbine remains clouded, with the several major automotive manufacturers having widely divergent commitments and activity in research and development. The most pessimistic viewpoints, of course, are that the above-mentioned costs of manufacture and sophistication of maintenance will negate potential for sales to the general public. (This is reflected in Table 28). The most optimistic viewpoints project that the gas turbine will almost totally supplant all other forms of automotive power by 2000 A.D. This will obviously be contingent upon major technological breakthroughs which will permit operation at increased pressures and temperatures, and with engine configurations less costly than existing turbine engines. Ceramic turbine wheels offer hope for this kind of breakthrough, but their development has not progressed enough to make a good estimate on their availability. It is noteworthy, too, that increasing pressures and temperatures may increase the probability of increased NO_x emissions. It remains to be seen, if NO_x is to be a serious problem with "automotive type" pressure ratio turbines of the future.

4. Stirling Engine

The Stirling external combustion engine is capable of operating on a broad range of fuels, and is insensitive to octane or cetane numbers. Fuel metering and mixing for efficient combustion is the only significant fuel tolerance problem to contend with. The Stirling will be in R&D and early production stages during 1976-1990 and will be designed to utilize those fuels expected to be generally available in 1985-2000. It is highly probable that (if diesel automotive engine technology and production accelerates during 1980-1990) Stirling production configurations will be designed around middle distillate fuels. Maximum projections for this engine indicate that it will take over no more than 10 percent of the light-duty automotive market by 2000 A.D. (again reflected in Table 28).

VI. PROJECTED GASOLINE COMPOSITION

The majority opinion of knowledgeable parties in the fuel production and automotive manufacturing industries is that the spark ignition engine will continue its dominant role until the year 2000, and will continue to require gasoline as a fuel. If syncrudes become available and are refined into gasoline, that gasoline's composition will be dictated by the engine technology of the time and not by the crude source.

Fuel refining experts believe that gasoline will change gradually over the next 10 years with the overall effect being small. The demand on the petrochemical market for propane and butanes will cause a gradual disappearance of these components from gasoline. The same can be said for benzene today and toluene will probably be reduced in the future for that reason also. Octane number is expected to be maintained in the 90-92 RON range, and manganese will probably find popularity as an octane improver even though not as capable as lead. Aromatics content of future gasolines will probably be maintained in the 25- to 30-percent range as a maximum. The loss of butanes and pentanes from the fuel will require increases in the C_6-C_7 range, thus altering the IBP and front-end curve. The midpoint and FBP will see little or no change.

After 1985, significant improvements in engine fuel metering systems can be expected. With computer-controlled "carburetion" and timing so that air-fuel ratios can be precisely maintained and varied as driving conditions and emissions dictate, new and more demanding specifications for gasoline will probably emerge. At that time, more narrow cuts of fuel will be required with more precise control of chemical composition and carbon-hydrogen ratios. Increased application of fuel injection systems would similarly place new requirements on gasoline composition. These requirements will not be met without additional costs, which must be borne by the consumer. High-volume production will minimize the cost increases, but it must be kept in mind that the more specific and stringent requirements become, the more expensive the product. If syncrudes are fed into the system, the costs will climb even more because of the increased costs of processing. The refiner is now under new pressure to provide finished fuels from the most efficient processes that result in the best overall energy yields. From this viewpoint, the best energy yield is accomplished when the finished fuel requires the least amount of refinery and crude energy. This, in turn, works against sophisticated "rework" processes which are expensive in energy as well as in dollars.

Experimental batches of gasolines and naphthas have been prepared from syncrudes derived from coal and oil shale. The data in Table 29 compare composition of gasoline from shale oil to petroleum-derived gasoline, and in Table 30 published data for syncrude naphthas are shown. Although in actual practice the snyfuels may have compositions completely different from those shown, these analyses do give an indication of what might be expected. The data also indicate that the composition of the naphtha is very dependent on coal or oil shale source and the liquefaction processes. The H-coal hydrogenation produced more 2^+ ring aromatic compounds than the COED pyrolysis, and the Wyoming

TABLE 29. COMPOSITION OF SYNTHETIC GASOLINE FROM THE PARAHO PROCESS

	Gasoline from Shale	Commercial Unleaded Gasoline
Parafins, vol %	44	34
Olefins, vol %	12	19
Naphthenes, vol %	8	18
Aromatics, vol %	36	29
Aromatic distribution, vol %		
Benzene	1.4	0.6
Toluene	7.0	2.1
Ethylbenzene	1.5	1.4
M&P Xylene	6.6	4.7
O-Xylene	2.5	2.4
C_9+ Aromatics	14.7	16.1
Oxygen, wt %	0.52	nil
Nitrogen, wt %	0.03	nil

TABLE 30. PROPERTIES AND HYDROCARBON COMPOSITION OF NAPHTHAS FROM SYNCRUDES

Source	Oil Shale, Wyoming	Oil Shale, Colorado	Bituminous Coal, Illinois	Bituminous Coal, Illinois	Subbituminous Coal, Wyoming
Liquefaction process	In Situ Combustion	Combustion Retort	COED, Pyrolysis	H-Coal, Hydrogenation	H-Coal Hydrogenation
Treatment of crude oil	Coked and Hydrogenated	Coked and Hydrogenated	Hydrogenated	---	---
Boiling range, °F	175°-350°F	180°-400°F	180°-390°F	C_4-400°F	C_4-400°F
Fraction of crude oil, vol %	22.4	34.5	33.1	33	57
Gravity, °API	52.6	51.3	43.8	49.2	50
Hydrogen, wt %	---	14.2	---	---	---
Nitrogen, wt %	0.0001	0.024	0.013	0.10	0.20
Sulfur, wt %	0.001	0.001	0.009	0.099	<0.07
Octane number, Research	---	32.8	70.1	---	---
Hydrocarbon type, wt %:					
Paraffins	42.8	47.7	7.1	12.0	18.9
Monocycloparaffins	43.4	34.5	58.9	47.9	44.5
Cycloparaffins, 2 rings		2.4	12.5	14.5	15.0
Alkyl benzenes	13.8	13.2	19.8	17.6	14.2
Aromatics, 2 rings		2.2	1.7	7.0	5.9
Nonhydrocarbons	<0.001	---	---	0.9	1.7

subbituminous coal produced naphtha with higher concentration of nitrogen compounds than the Illinois bituminous. It is anticipated that the last two naphthas would be refined further to remove nitrogen and 2 ring aromatic compounds before using in gasoline blending.

VII. ACKNOWLEDGEMENTS

As has been stated, all of the foregoing projections have been based upon the author's interpretation of subject matter covered during personal interviews with technical personnel recognized as currently active and highly competent in the oil shale, coal, refining, and automotive industries. In all, about 75 individuals were contacted in face-to-face discussions. While each interviewer cannot properly be identified individually, the authors wish to express their gratitude for the uniform and consistent degrees of candor, clarity and objectivity exhibited by this most knowledgeable group. The list of individual organizations from which these persons were selected is given below. *This listing is not intended to imply that any statements made in this report represent the policies or opinions of any given organization.* Rather, the authors have made an effort to reflect prevailing opinions in a technological area which changes so rapidly that specific statements may be refuted tomorrow—and again accepted the day following.

Consultants

- Cameron Engineers, Incorporated
- University of Wisconsin, Department of Mechanical Engineering
- Stanford Research Institute

Automotive

- General Motors Research Center
- Ford Development Center
- Chrysler Engineering

Energy (Government)

- ERDA, Fossil Fuels, Washington, D.C.
- ERDA, Bartlesville Energy Research Center

Energy (Industry)

- SOHIO Research & Development Division
- Brown & Root Engineering
- Shell Oil Company
- EXXON Research & Development Center
- Fluor Corporation
- SASOL, South Africa
- Charter Oil International
- Pennzoil United

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